Cellulose, so much more than paper

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While cellulose is one of the most exploited natural resources on the planet and serves mankind throughout its entire history for construction, clothing and paper, it is only in the last decades that it revealed its full potential as a functional material for photonic applications.[1–3] In nature, cellulose has been long ago employed by the plant realm to provide mechanical strength, stiffness and toughness to biological tissues, but also as the key building blocks of sophisticated tissues with amazing optical properties. In several species, helicoidal architectures of cellulose are observed in the secondary cell wall of different plant tissues and provide incredibly bright colourations to their fruits or leaves.[4–8]

In the visible range, cellulose behaves as a transparent, dielectric, birefringent material, yet the value of its refractive index and birefringence strongly depend on its configuration, similarly to many other biopolymers.[9,10] The generic term "cellulose" indeed summarises a wide diversity of materials displaying a variety of conformations and thus optical responses. Natural cellulose comes in hierarchical fibrillar form and consists of glucose polymer chains stabilised *via* hydrogen bonds and hydrophobic interactions.[11] The native fibres hugely vary in size, crystal structure and crystallinity, depending on their biological origin. Mechanical or chemical treatments of these fibres allows producing mainly two types of cellulose nanomaterials: cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs).[12–14] As they partially retain the semi-crystalline nature of native cellulose, they both display high values of intrinsic birefringence and refractive index ($\Delta n \approx 0.074\text{-}0.08$),[9,15] while their high aspect ratio contributes to an even higher extrinsic birefringence when dispersed in a medium of lower optical index such as water ($\Delta n/\Phi \approx 0.12$, where Φ is the volume fraction of cellulose).[15,16] Native fibres can also be chemically modified and functionalised to produce stable solutions of individual polymer chains, so-called cellulose derivatives, for which the refractive index and birefringence may be smaller,[17,18] but remains comparable to soft materials used in photonics. When compared to other biopolymers and proteins, cellulose abundance and high refractive index make it an ideal material to produce next generation optical materials, especially when it comes to sustainability and bio-compatibility. Cellulose nanomaterials are for these reasons an industrial reality: the last decade has seen an increasing number of companies selling nano-cellulose products and research groups working towards the development of cellulose-based optics and photonics have consequently flourished.

Recently, considerable efforts have been provided in the development of CNC-based optical materials. The understanding of their cholesteric liquid crystalline behaviour in suspensions, observed for the first time in the early 90s,[19] enabled only nowadays a good control of the optical response of photonic cellulose nanocrystal-based film. In analogy to liquid crystal molecules, these bio-sourced rod-like colloids spontaneously form, above a critical concentration, a chiral nematic structure whereby individual CNCs align along a helicoidally birefringent superstructure. This organisation can be maintained in the dry state upon

solvent evaporation, and it gives rise to strong reflection peaks.[1] The reflected wavelengths and the scattering properties of these films therefore depend on both the orientation of the cholesteric domains and the value of the pitch in the films.[20,21] Recently, these features were found to be determined by the morphology of the mesophase at the kinetic arrest (including cholesteric droplets called tactoids[22–24]) and the subsequent distortion that occurs as the superstructure is vertically compressed upon drying.[20,21]

While the chiral nature of such blocks is still a matter of debate,[25] the chirality of the cellulose nanocrystals films is always left-handed.[24] Instead, cellulose derivatives can self-assemble with both handedness.[26] Coloured cholesteric films from cellulose derivatives can also be obtained,[27–29] and in laminates they proved suitable as low-cost and scalable mechano-chromic sensors for pressure mapping as they are compatible with roll-to-roll processing.[18,30] On a different note, cellulose derivatives can also be directly patterned at the nanoscale *via* focused electron beam-induced conversion to fabricate cellulose-based nanostructured materials.[31]

However, as any biologically sourced material, cellulose nanocrystals can be batch-sensitive as their properties are related to the source and the methodology of extraction. While huge efforts have been done by the community to improve standardisation, significant differences in the characteristics of the material are still found in commercially available sources, and several challenges still need to be addressed for a wide exploitation of this resource into commercial applications.[14,32]

One of the current challenges in the exploitation of cellulose nanocrystals is controlling their size and shape polydispersity.[3] As the phase separation from isotropic to chiral nematic during the self-assembly is connected to the aspect ratio of the nano-crystals,[33] the polydispersity causes size fractionation within the assembly, leading to segregation within the films.[34–36] This issue can be addressed on lab-scale with the use of external fields or by increasing the evaporation times but it is not trivial when it comes to industrial scale up.[24] A possible solution to this challenge is represented by moving away from films and control the assembly in confined geometries where various levels of structuration can be achieved at different length scales.[37,38] Moreover, the unique combination of chemical, mechanical and optical properties of these biologically sourced building blocks encouraged the community to develop their utilisation in a broad range of applications: from printing and sensing,[38] to their use as mesoporous chiral nanotemplates or highly scattering materials, to name just a few.[39,40]

As for cellulose nanocrystals, cellulose nanofibrils have been exploited on large scale and there is a huge literature on the preparation and fabrication of highly optically transparent cellulose nanofibril films (or “nanopapers”),[41,42] which are also available commercially for flexible displays, electronic and solar cells, but also for packaging.[43] Roll-to-roll compatible production processes have been in fact already established to fabricate films with different optical properties from fully transparent to opaque ones.[44,45] The intrinsic high value of anisotropy of cellulose fibrils in terms of refractive index and aspect ratios shape makes them also very suited for highly scattering materials. The optical properties of membranes composed of cellulose nanofibrils can achieve highly bright white, even in thin coatings. This is extremely relevant for industrial applications as commercially available white products,

such as paints and sun creams, are typically formulated with high refractive index nanoparticles (e.g. TiO_2) as scattering enhancers, which had recently raised serious health and environmental concerns.[46]

Nature has been a tremendous source of inspiration when it comes to photonics. From light management in photosynthetic systems to control of appearance in living organisms, we can now look at nature not only for optical design strategies, but also for material exploitation: cellulose functionalities can be now engineered for optics and photonics in plants and bacteria. Moreover, as the most abundant bio-polymer on the planet, cellulose represents a truly renewable and biodegradable source for the manufacturing of sustainable products, especially nowadays in the context of growing microplastic pollution concerns worldwide.[47,48]

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Panel Figure: Artistic view of the hierarchical structuration of cellulose-based tissues in plants (*Credits: Nicolò Mingolini*).

Figure 1: **Cellulose photonic structure for controlling appearance**. The blue colour visible in the leaves and fruit are obtained with helicoidal cellulose architecture in the cell wall of the epidermal cells of the plants. A- Coloured leaves from *Microsorum thailandicum, B-Pollia Condensata* and C-*Magaritaria Nobilis.*

Figure 2: **Cellulose based Photonic structures**. A- Coloured flexible film obtained with cellulose nanocrystals. B- Multicolour printed microfilms of cellulose nanocrystals, the reflected light is circularly polarised so the colour is visible only in the circular left polarisation channel. C,D- Transparent and opaque cellulose nanofiber films and respective SEM in E,F showing that different morphology of the fibres leads to differe light transport properties. G- Roll-to-roll photonic Cellulose laminate.

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